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A hybrid encapsulation method for organic electronics

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We report a thin-film encapsulation method for organic electronics that combines the deposition of a layer of SiO_x or SiN_x (100 nm) by plasma enhanced chemical vapor deposition followed by a layer of Al_2O_3 (10–50 nm) by atomic layer deposition and a 1-μm-thick layer of parylene by chemical vapor deposition. The effective water vapor transmission rates of the encapsulation was $(2\pm1)\times10^{-5}$ g/m^2 day at 20 °C and 50% relative humidity (RH). The encapsulation was integrated with pentacene/C_{60} solar cells, which showed no decrease in conversion efficiency after 5800 h of exposure to air demonstrating the effectiveness of the encapsulation methodology. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3115144]

The development of encapsulation methods is seen as a critical technology to enable the long term stability and deployment of organic electronic devices. While sealing devices with glass or metal lids has been used for encapsulation, increased attention has been paid to the development of high-quality thin-film encapsulation methods due to their flexibility along with high barrier performance. Such films are often created using high-quality single layer inorganic films or alternating multilayers consisting of organic and inorganic materials. In all, these materials have demonstrated effective water vapor transmission rates (WVTRs) ranging from 10^{-4} to 10^{-6} g/m^2 day.[1,2] However, their complex architecture and/or the long processing times have proven to be barriers themselves to their integration in actual devices. Overall, it is desirable to develop vacuum deposition methods for thin-film encapsulation, which reduces the complexity and processing time, while providing high-quality films that are scalable to large areas.

Plasma enhanced chemical vapor deposition (PECVD) processing of inorganic films is one of the techniques which allows for industrial-scale deposition of coatings with good deposition rates at relatively low deposition temperatures.[3] However, most thin-films deposited by PECVD have defects which provide permeation pathways for water vapor and oxygen. Therefore, most single layer films deposited by PECVD cannot satisfy the stringent encapsulation requirements of organic devices and are often used in complex multilayer architectures. Other methods such as atomic layer deposition (ALD) are amenable to inorganic coatings, creating smooth, conformal, and pinhole-free films which are highly desirable for encapsulation. However, the deposition rate for ALD films is typically an order of magnitude lower than PECVD processing, resulting in very long deposition times.[4,5]

Here, we report on a hybrid thin-film encapsulation method for organic electronics that combines the deposition of a layer of SiO_x or SiN_x (100 nm) by PECVD followed by a layer of Al_2O_3 (10–50 nm) by ALD and a 1-μm-thick layer of parylene by CVD as protective layer. Films of SiO_x were deposited using SiH_4 and N_2O, while SiN_x films were deposited using SiH_4, He, N_2, and NH_3 using a Plasma-Therm PECVD system. A rf power of 30 W and deposition temperature of 110 °C were utilized for compatibility with organic electronic devices,[6] providing a deposition rate of 33 and 10 nm/min for SiO_x and SiN_x, respectively. After fabrication of the PECVD deposited films, samples were transferred to an ALD chamber, and Al_2O_3 was deposited at 110 °C using a Savannah 100 ALD system by Cambridge NanoTech. The pulse duration was 15 ms for both trimethylaluminum and water, and nitrogen was purged for 5 s between pulses, giving a deposition rate of 0.5 nm/min. Finally, parylene was deposited by CVD on top of the hybrid layer at room temperature (Laboratory Coater PDS2, Specialty Coating Systems). The top parylene layer was utilized to keep water from condensing on the Al_2O_3 film layer which can cause corrosion of the film.[6]

The barrier performance of the hybrid film was investigated using the Ca corrosion test by monitoring changes in the electrical conductance of encapsulated Ca sensors. In this experiment, we used a 4.5×7 mm^2 Ca sensor and Al interconnects for resistance measurements. To create the Ca test structure, aluminum (100 nm) and calcium (300 nm) layers were deposited through shadow masks on glass substrates using thermal evaporation. After deposition, the Ca samples were transferred to a PECVD system. A 400 nm PECVD SiO_x buffer layer was first deposited to planarize the Ca sample and help reduce side permeation effects [Fig. 1(a)]. Next, the hybrid encapsulation layer was deposited to form the barrier. This was done by depositing 100 nm of either SiO_x or SiN_x followed by 50 nm of Al_2O_3 and a 1-μm-thick layer of parylene. Encapsulated Ca sensors were stored in an environmental chamber at 20 °C and 50% RH and the effective WVTR was then measured by monitoring the conductance change in the Ca sensor at least for 800 h. The change in conductance as a function of time is linear, as shown in Figs. 1(b)–1(d), and the slope dG/dt is used to calculate effective WVTR values according to

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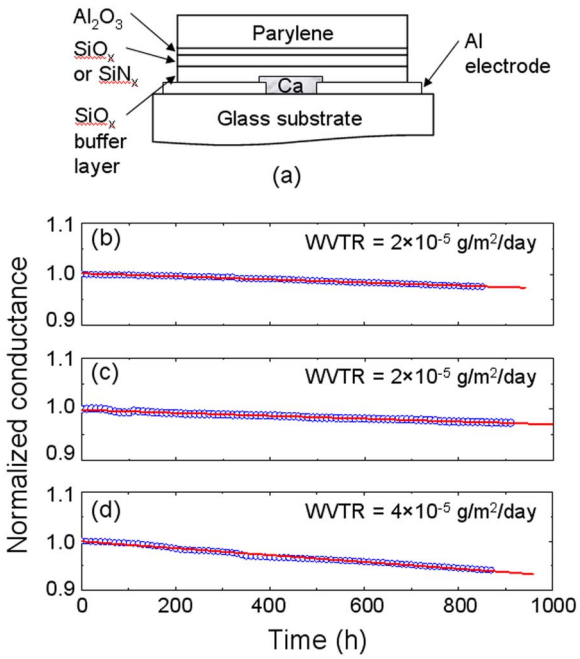

FIG. 1. (Color online) (a) Structure of the hybrid encapsulation layer consisting of a 400-nm-thick SiO_x buffer layer for preventing side permeation, a 100-nm-thick layer of SiO_x or SiN_x and 50 nm Al_2O_3, and a 1-μm-thick parylene layer. [(b)–(d)] Normalized change in electrical conductance of Ca sensors with three different encapsulation geometries as a function of time; (a) SiO_x(100 nm)/Al_2O_3(50 nm)/parylene (1 μm), (b) SiN_x(100 nm)/Al_2O_3(50 nm)/parylene (1 μm), and (c) SiO_x(100 nm)/Al_2O_3(10 nm)/parylene (1 μm). In all geometries, the Ca sensor was first coated with a 400-nm-thick SiO_x buffer layer. Symbols are experimental data and solid lines are linear fits.

$$\mathrm{WVTR}[\mathrm{g/m^2\ day}] = -n \times \delta_{\mathrm{Ca}} \times \rho_{\mathrm{Ca}} \times \frac{dG}{dt} \times \frac{l}{w} \times \frac{M(\mathrm{H_2O})}{M(\mathrm{Ca})} \times \frac{\mathrm{area(Ca)}}{\mathrm{area(window)}}, \quad (1)$$

where n is the molar equivalent of the degradation reaction which is assumed as $n=2$ from the chemical reaction of Ca with water [$\mathrm{Ca+2H_2O}(n=2) \rightarrow \mathrm{Ca(OH)_2+H_2}$].[7] In Eq. (1), δ_{Ca} and ρ_{Ca} are the Ca resistivity (3.4×10^{-8} Ω m) and density (1.55 g/cm^3), [7] $M(\mathrm{H_2O})$ and $M(\mathrm{Ca})$ are the molar masses of water (18 amu) and of Ca (40.1 amu), and l and w are the length and width of Ca sensor, respectively. The ratio of the area of the Ca sensor to the area of the window for water permeation and the ratio of the length is unity due to the geometry of the experimental setup. Three identical Ca sensors were tested for each encapsulation structure, such that reported WVTR values were averaged over three devices.

The SiO_x/Al_2O_3/parylene and SiO_x/Al_2O_3/parylene barrier films yielded effective WVTR values of $(2\pm1)\times10^{-5}$ and $(3\pm2)\times10^{-5}$ g/m^2 day, respectively. While multilayer films containing SiN_x deposited by PECVD have been reported to show better barrier performance than SiO_x,[8,9] our results show that there is no significant difference between the two films when utilized in the hybrid structure. These results suggest that the water permeation through the defects and pinholes in both SiO_x and SiN_x films are well passivated by the Al_2O_3 layer, providing a barrier film with performance similar to multilayer encapsulation but with a far simpler architecture. Additional Ca corrosion tests carried out on Al_2O_3 (100 nm)/parylene (1 μm) films and SiO_x (100 nm)/parylene (1 μm) yielded an effective WVTR value of $(1\pm0.3)\times10^{-4}$ and $(4\pm0.2)\times10^{-2}$ g/m^2 day, respectively. Based upon the calculation of lamination theory,[10,11] the effective WVTR of the two films combined is expected to be on the order 10^{-4} g/m^2 day, which is one order of magnitude higher than that of actual measured value. The lower permeation rate of the hybrid film is believed to have originated from the passivation of defects in the SiO_x layer by the Al_2O_3 layer. Such synergistic effects have been reported in the cases of interlayers between inorganic and organic multilayer encapsulations as well as in ALD deposited Al_2O_3 on SiO_x and ALD deposited Al_2O_3on ZrO_2.[12–14] One possible explanation is that this interlayer region induces an additional rate-limiting permeation step resulting in a lower permeation rate than those of either single SiO_x or Al_2O_3. It should be noted that WVTR measurements showed no increase in permeation rates during the Ca corrosion tests which lasted for a minimum of 800 h. This suggests that the parylene layer is effective in preventing condensed water-induced corrosion of the Al_2O_3 film. Without the parylene layer, corrosion of the Al_2O_3 layer was observed within the first 200 h resulting in a sharp rise in WVTR.

Additional studies on the hybrid films were performed by reducing the thickness of the Al_2O_3 to determine its impact on the effective WVTR and defect passivation performance. By decreasing the thickness of the ALD layer to 10 nm, the effective WVTR of SiO_x based hybrid film was $(4.0\pm0.5)\times10^{-5}$ g/m^2 day. Therefore, a 10-nm-thick Al_2O_3 film deposited by ALD was enough to seal the defects and pinholes in the SiO_x film, reducing the overall processing time. With a deposition rate of 0.5 nm/min for the Al_2O_3 layer along with a deposition rate of 33 nm/min for the SiO_x layer (three times faster than that of SiN_x), this hybrid encapsulation architecture provides a good combination of barrier performance and reduced processing time when compared to some multilayers with similar permeations rates. This is afforded by utilizing a fast deposition of PECVD processing and minimizing the deposition time needed for ALD processing, especially when the 10-nm-thick layer is used. Overall, we have observed a decrease in processing time of a factor of 5 when compared to the multilayer structure consisting of SiO_x/parylene with similar effective WVTR values which we have produced.

After evaluation of the permeation rates of the barrier films, their performance was evaluated through the encapsulation of pentacene/C_{60} organic solar cells. The organic solar cells were fabricated on glass substrates as previously reported[15] with a geometry of indium tin oxide/pentacene (50 nm)/C_{60} (45 nm)/bathocuproine (7 nm)/Al and an active are of ~0.1 cm^2. First, a 400-nm-thick buffer layer of SiO_x was deposited on top of the solar cells. Then, the samples were encapsulated with SiO_x/Al_2O_3/parylene and SiN_x/Al_2O_3/parylene hybrid films with thicknesses of 100 nm/50 nm/1 μm, respectively. To study the impact of the encapsulation process on the organic solar cells, the electrical characteristics of the devices were measured before encapsulation and right after in a nitrogen environment. A 175 W xenon lamp (ASB-XE-175EX, CVI) was used as a broadband light source with an irradiance of ~73 mW/cm^2. Then, the encapsulated devices were stored for extended periods of time in an environmental chamber (20 °C, 50%

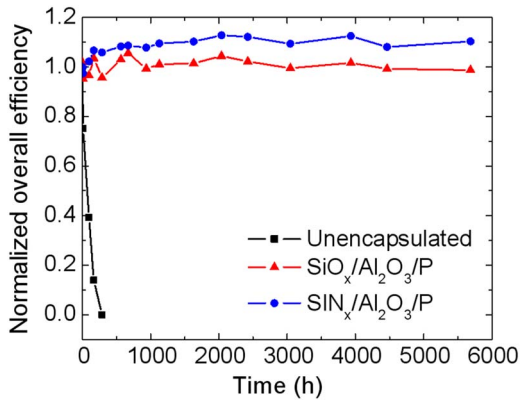

FIG. 2. (Color online) Normalized power conversion efficiency as a function of time of pentacene/C_{60} solar cells encapsulated with a 400-nm-thick buffer layer of SiO_x and different encapsulation layers with geometries SiO_x(100 nm)/Al_2O_3(50 nm)/parylene (1 μm) (circles), SiN_x(100 nm)/Al_2O_3(50 nm)/parylene (1 μm) (triangles), and a reference sample without encapsulation (squares).

RH). The electrical characteristics were measured periodically in the laboratory environment under a solar simulator (91169, Oriel) to investigate device degradation as a function of time. Three identical solar cells were tested for each encapsulation. The performance averaged over three devices was then compared to that of a bare unencapsulated sample used as a reference device.

The power conversion efficiency η increased from $3.2\% \pm 0.1\%$ to $3.4\% \pm 0.1\%$ after encapsulation due to the thermal annealing effects, as reported previously.[16] Figure 2 shows the normalized η as a function of exposure time for the two different types of hybrid encapsulation and for a reference sample without encapsulation. While the efficiency of the unencapsulated device degraded very rapidly, those of encapsulated devices remained unchanged with over 5800 h of exposure. These results show that encapsulation films with effective WVTRs on the order of 10^{-5} g/m^2 day are sufficient for protecting the shelf lifetime of pentacene/C_{60} solar cells. This test also validates the effectiveness of the hybrid thin-film encapsulation method in protecting organic electronic devices.

In summary, a hybrid encapsulation architecture that combines inorganic films deposited by PECVD and ALD was demonstrated to have an effective WVTR as low as $(2 \pm 1) \times 10^{-5}$ g/m^2 day. The deposition of the hybrid coating results in a film which is superior to any of the individual component films, showing the synergistic effect of this architecture. The compatibility and effectiveness of this structure was successfully validated on pentacene/C_{60} organic solar cells. The hybrid approach presented here combines simplicity, low effective WVTR values, and reduced processing times in order to provide an efficient encapsulation architecture for organic electronic devices. All tests in this report have been performed at 20 °C and 50% RH in order to test the devices under the same conditions as the Ca tests, providing shelf lifetime studies under a known permeation rate. In addition, higher temperature exposures of pentacene/C_{60} samples for a long period of time can cause additional changes to the device performance. Thus, testing at room temperature provided a method to isolate changes due to the potential negative impact of water vapor and oxygen permeating through the encapsulation. Additional testing is now underway to test the encapsulation at higher temperatures to test its viability under harsh conditions.

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